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# DEVELOPMENT, FABRICATION AND TESTING OF A PPB COPPER ANALYZER

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Dow Chemical Company

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# DEVELOPMENT, FABRICATION AND TESTING OF A PPB COPPER ANALYZER

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16. *Abstract* A parts per billion (PPB) total copper analyzer has been developed, fabricated and tested. Samples from desalination plant waste streams contain copper in three distinct forms, ionic, complexed, and particulate, all of which must be converted to a common form for colorometric analysis of "total" copper. Acid conversion is the most common method with hydrofluoric being preferred over hydrochloric or nitric. The addition of colorimetric reagent results in a colored complex, the amount of color being a function of copper concentration. The amount of color as determined spectrophotometrically is related to the "total" copper concentration in the sample stream. Field testing of the completed analyzer under actual and experimental desalting plant conditions has shown it to be a highly reliable and accurate instrument when compared to actual laboratory copper analyses by conventional methods. (OWRT)



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## SECTION I. INTRODUCTION

Unless careful water chemistry controls are observed, copper can be a major contaminant in the brine effluent streams in the desalting of seawater and brackish water. This is of special significance in the widely used distillation processes which have historically employed substantial quantities of copper alloys. The corrosion of copper alloys occurring because of unsuitable water chemistry conditions causes copper to manifest itself in the effluent stream in three general forms: ionic, complexed, and particulate.

Studies have indicated that the recommended water quality criterion for copper is a concentration in the low parts-per-billion range. The problem lies in the measurement of "total" copper in such a small concentration range on a continuous basis.

Several methods for measuring such low concentrations are known, but most have serious drawbacks, especially for continuously monitoring "total" copper. The work described in this report pertains to the development of a colorimetric copper analyzer for continuous measurement of "total" copper in very low concentrations.

## SECTION II. SUMMARY AND CONCLUSIONS

Samples encountered in seawater desalting systems contain copper in three distinct forms. In order to analyze for "total" copper, it is necessary to first convert all three forms to a common one for colorimetric analysis, the method of choice for accurate determination of the copper present. Following this conversion of copper to a common form, it is necessary to filter the sample in order to provide a completely clear solution for colorimetric analysis. Following these steps, pH adjustment and addition of the necessary colorimetric reagent results in a colored complex, the amount of color being a function of copper concentration. The amount of color is determined spectrophotometrically and related to the "total" copper concentration in the sample stream.

Extensive laboratory and field efforts toward development of a parts-per-billion "total" copper analyzer based on the above scheme, shown graphically in Figure II-1, have led to the following conclusions:

1. In compliance with the technical objectives of this contract, the development, fabrication, and testing of a PPB total copper analyzer has been successfully completed. The completed continuous "total" copper analyzer system is shown by the photograph, Figure II-2.

2. Field testing of the completed analyzer under actual and experimental desalting plant conditions has shown it to be a highly reliable and accurate instrument when compared to actual laboratory copper analyses by conventional methods (Table IV-I, p. 30).

3. Acid conversion of the three forms of copper to a common form is the most practical method. Of the acids tested, the order of effectiveness is hydrofluoric, hydrochloric, nitric, with hydrofluoric acid being by far the best.

4. Improved conversion rates are related to increased contact time and elevated temperature.

5. The addition of acid above the stoichiometric amount required to lower sample acidity to pH 2 has little effect on the conversion rate.

6. An alternate proposed method for conversion of the three forms of copper to the complexed form using

Figure II-1

SIMPLIFIED COPPER ANALYZER FLOW DIAGRAM

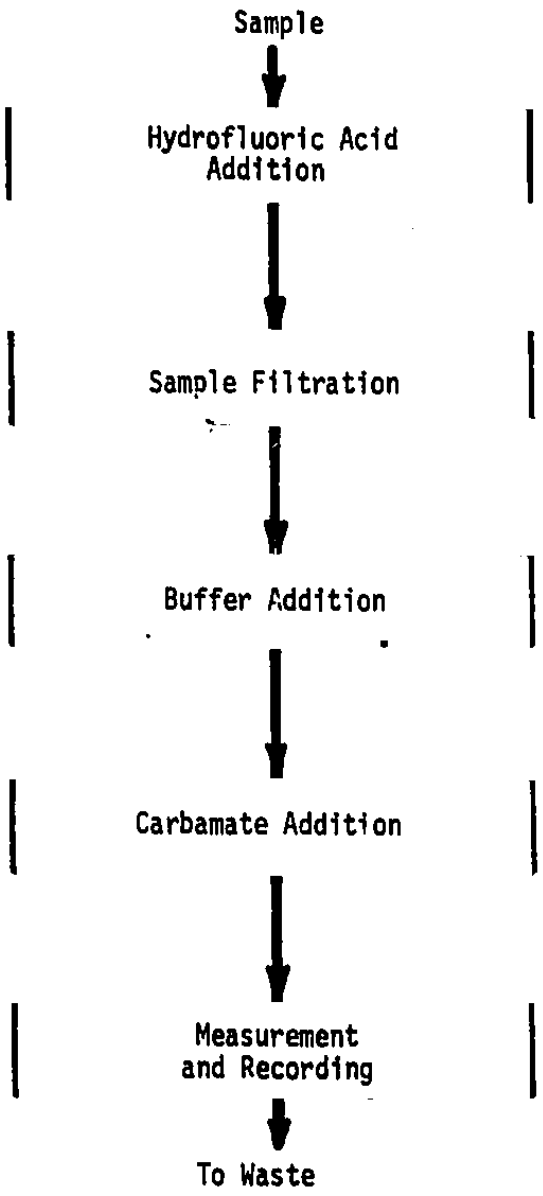
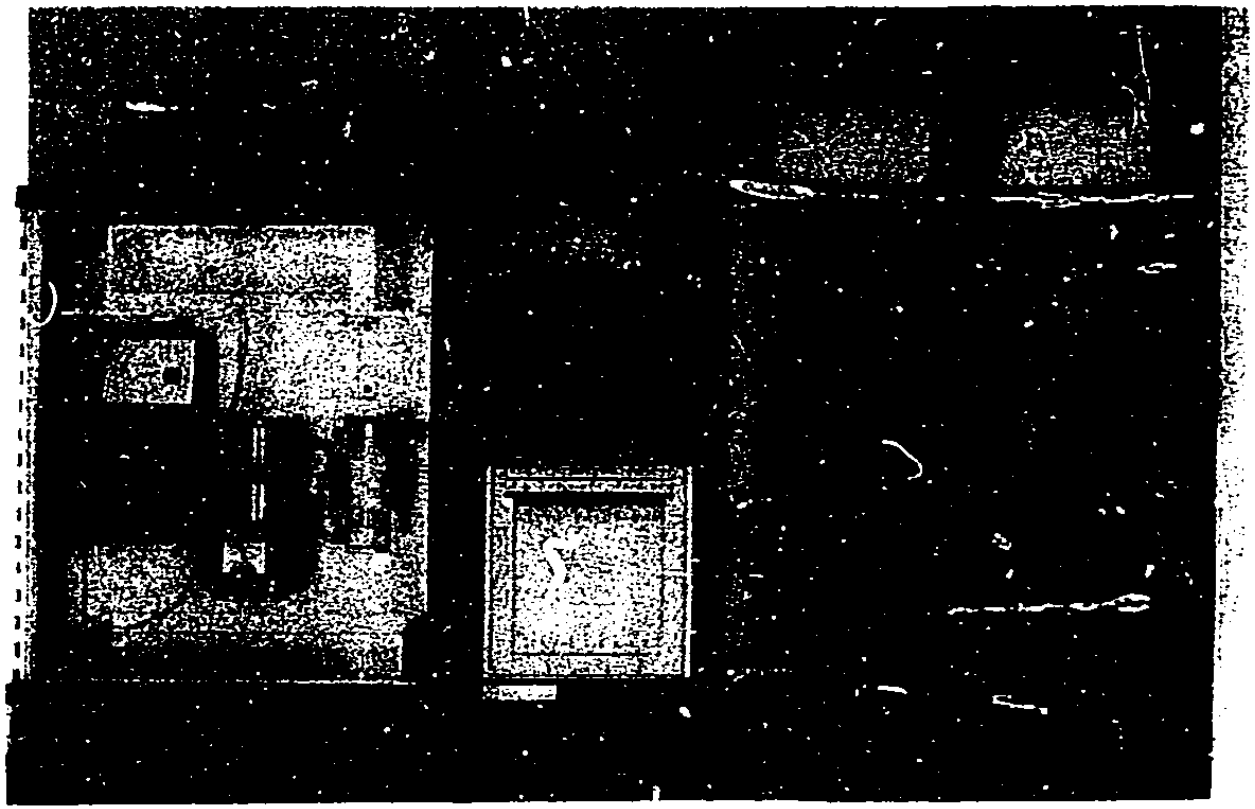


Figure II-2

PHOTOGRAPH OF COMPLETED ANALYZER



iron-ethylenediaminetetraacetate (EDTA) plus excess EDTA was not practical. The absorption of light by the blue copper-EDTA complex was too low to make the process sufficiently sensitive for colorimetric determination at low copper levels.

7. The use of the diethanoldithiocarbamate colorimetric analysis method for determination of copper was found to be pH-dependent. The most intense color is exhibited at pH 3. Above pH 6 the color intensity is constant and does not vary with pH. Between pH 3 and 6, color intensity falls off slightly with increasing pH.

8. The addition of pyrophosphate to tie up the iron or a suitable buffer to increase the pH to 5 or 6 eliminates an iron interference to the carbamate colorimetric analysis method.

9. It was found that addition of pyrophosphate or most buffers to hydrofluoric acid treated seawater causes a turbid sample condition to develop due to a calcium-magnesium-fluoride complex precipitating from solution. Addition of the proper citrate buffer solution prevents the iron interference and does not cause turbidity in the sample.

10. The method chosen to "instrument" the acid injection was found to be effective and convenient. Minor plugging problems due to silica in the sample were corrected by judicious use of Teflon® parts and careful placement of the acid entrance point.

## SECTION III. TECHNICAL PROGRAM

### A. Acid Conversion Studies

#### 1. Experimental Method

In order to study the effect of various acids on conversion of the three forms of copper to a common form, a laboratory procedure was devised which would allow variation in the parameters to be investigated.

A suitable size portion of sample was heated in a sealed flask until the required temperature had been attained. At this time sample aliquots were withdrawn for analysis of the three forms of copper. The remainder of the sample was acidified, the flask again sealed, and kept "on temperature" for a specified time, using constant agitation via a magnetic stirrer. At the end of this time interval, aliquots were again withdrawn for analysis of the three forms of copper. All copper analyses were performed by the colorimetric neocuproine method detailed in Appendix A.

After the first few trial runs, it was noticed that a different "total copper" was found before and after sample treatment. Usually the aliquots drawn after acid treatment showed a higher "total copper" than the aliquots drawn before acid treatment. Analysis of the acid being used did not show enough copper to account for this difference.

It was finally established that this difference in "total copper" before and after acid treatment was caused by:

- Small amounts of copper introduced with the acid.
- Copper being "plated out" on the walls of the flask followed by redissolving after acid addition.
- Inaccuracy of the colorimetric neocuproine copper analysis method.

During this work, it was found that the neocuproine copper analysis method accounts for most of the error. The method is only accurate to about ±5% of the amount of copper present. Since the work involved samples containing a large amount of particulate copper and since the amount of this copper converted

to the ionic form was quite large, it is believed that the small difference in copper material balance before and after sample treatment could be tolerated.

2. Hydrochloric Acid

Using the foregoing method, hydrochloric acid was tried for conversion of the particulate copper to the ionic form. Figure III-1 shows the effect of HCl at two different temperatures at various contact times. Notice that at a low temperature (75°F) an increase in contact time improved the rate of conversion up to a point. Contact times in excess of 10 minutes did not seem to improve the conversion. At a higher temperature (150°F) the contact time had little effect on the conversion rate.

Since it is desirable to keep the contact time to a minimum in order that the analyzer might quickly respond to a change in copper concentration, it was decided that a 5-minute contact time would be a reasonable compromise between conversion rate and analyzer response time. Figure III-2 illustrates the effect of temperature on HCl conversion rate at a constant contact time of 5 minutes and 1 ml. of concentrated HCl per 100 ml. sample. Notice that the conversion rate rapidly increases as the sample temperature is increased, and probably reaches 100% just above 150°F.

Results with HCl indicate that it is effective for conversion of particulate to ionic copper to about 80% conversion. If higher temperatures are required to increase the conversion, its desirability for inclusion into a copper analyzer would be lessened.

3. Nitric Acid

In a similar manner, nitric acid was used for attempting the conversion of particulate to ionic copper. The general results found for HCl were also seen when using $HNO_3$, although HCl seems to be somewhat more effective. Rates of conversion from 40 to 60% were observed, compared to 20 to 80% under similar conditions when using HCl. Since nitric acid is more hazardous than hydrochloric, no further work was done on the use of this material.

Figure III-1

EFFECT OF TIME ON HCl CONVERSION OF PARTICULATE TO IONIC COPPER AT TWO DIFFERENT TEMPERATURES

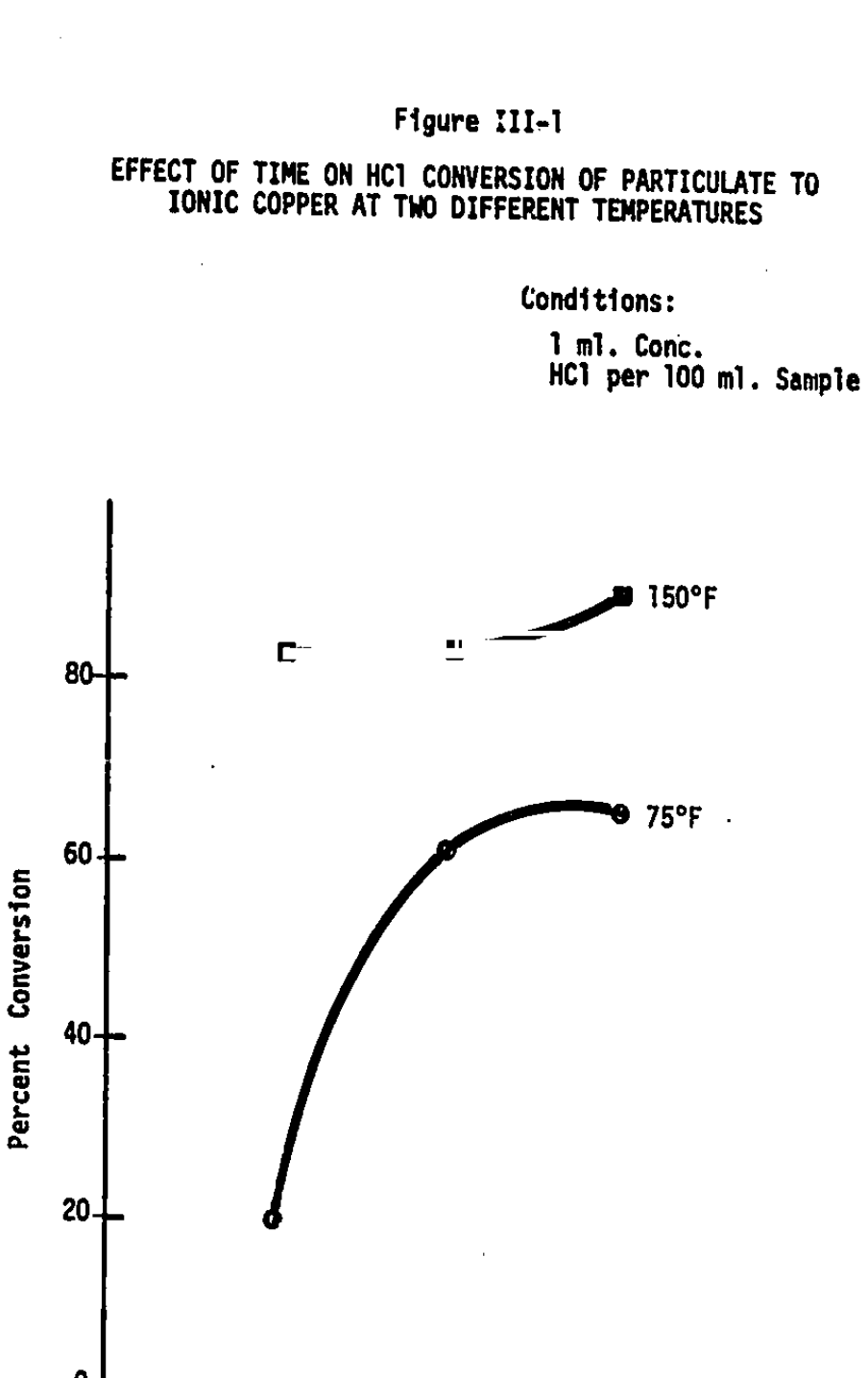
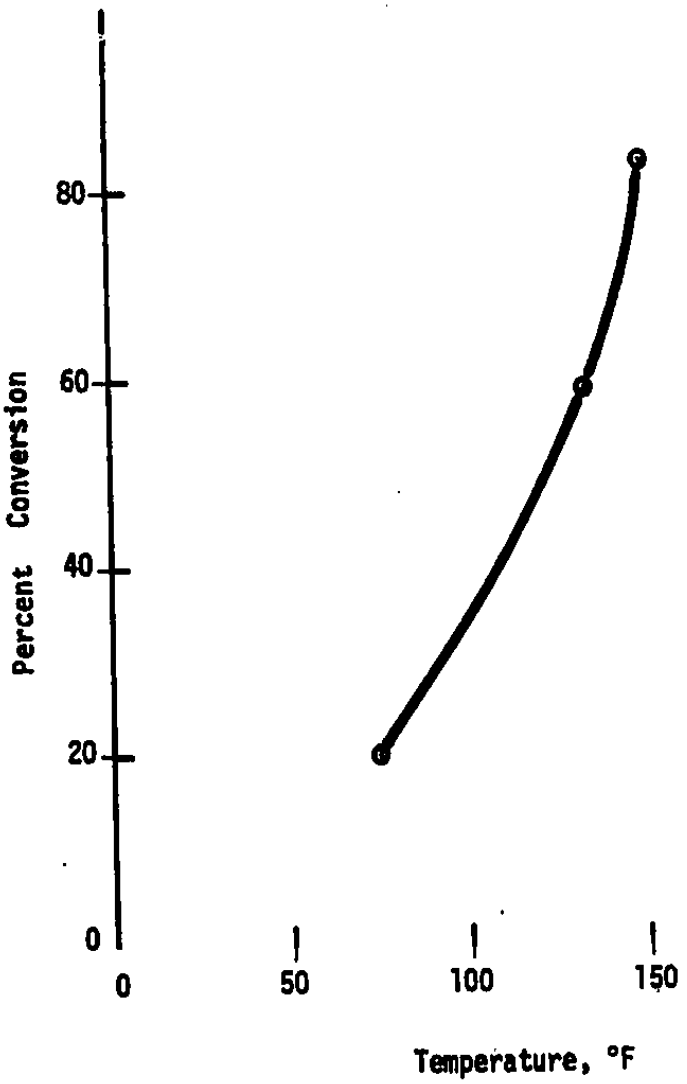


Figure III-2

EFFECT OF TEMPERATURE ON HCl CONVERSION OF PARTICULATE TO IONIC COPPER

Conditions:

1 ml. Conc.
HCl per 100 ml. Sample
5 minute contact time



4. Hydrofluoric Acid

The effects of hydrofluoric acid (HF) on particulate copper were studied by the method already described. Results were quite promising. Low concentrations of HF at low temperature and at higher temperatures showed that the most critical parameter is the length of contact with the particulate matter. Figure III-3 illustrates the effect of contact time at 150°F. Notice that almost complete conversion of the particulate copper has been obtained. Experiments at room temperature and 5 minutes contact time showed 90% conversion. A test at room temperature and a contact time of 5 minutes with a ten-fold reduction in HF concentration showed 80% conversion of the particulate copper.

These results indicate that hydrofluoric acid is the preferred reagent for conversion of the copper to a common form prior to colorimetric analysis.

B. Iron-EDTA Conversion

Another method proposed to convert the three forms of copper to a common form was the use of iron-EDTA plus excess EDTA. This method is based on the premise that iron-EDTA should oxidize the particulate copper to the ionic form. The excess EDTA should then chelate this ionic form plus the originally present ionic copper, converting all the copper into the complexed form.

In an effort to study this method of copper conversion, a solution was made containing 0.05 molar iron-EDTA complex and 0.05 molar excess EDTA in ammoniacal form. This reagent will be referred to as the "EDTA Reagent."

Using the experimental method previously described, samples were analyzed before and after treatment with the "EDTA Reagent." For simplicity, the decrease in particulate copper was determined. The effects of "EDTA Reagent" concentration, contact time, and temperature were studied. It was found that an increase in any one variable increased the rate of copper conversion, with all three variables showing about the same overall effect. Figure III-4 shows the effect of temperature on the conversion rate. At 150°F the particulate copper has decreased by 89%. The rate is 96% under the same conditions except for a contact time of 12 minutes.

Figure III-3

EFFECT OF TIME ON HF CONVERSION OF PARTICULATE COPPER

Conditions:

1 ml Conc.
HF/100 ml. Sample
Temperature = 150°F

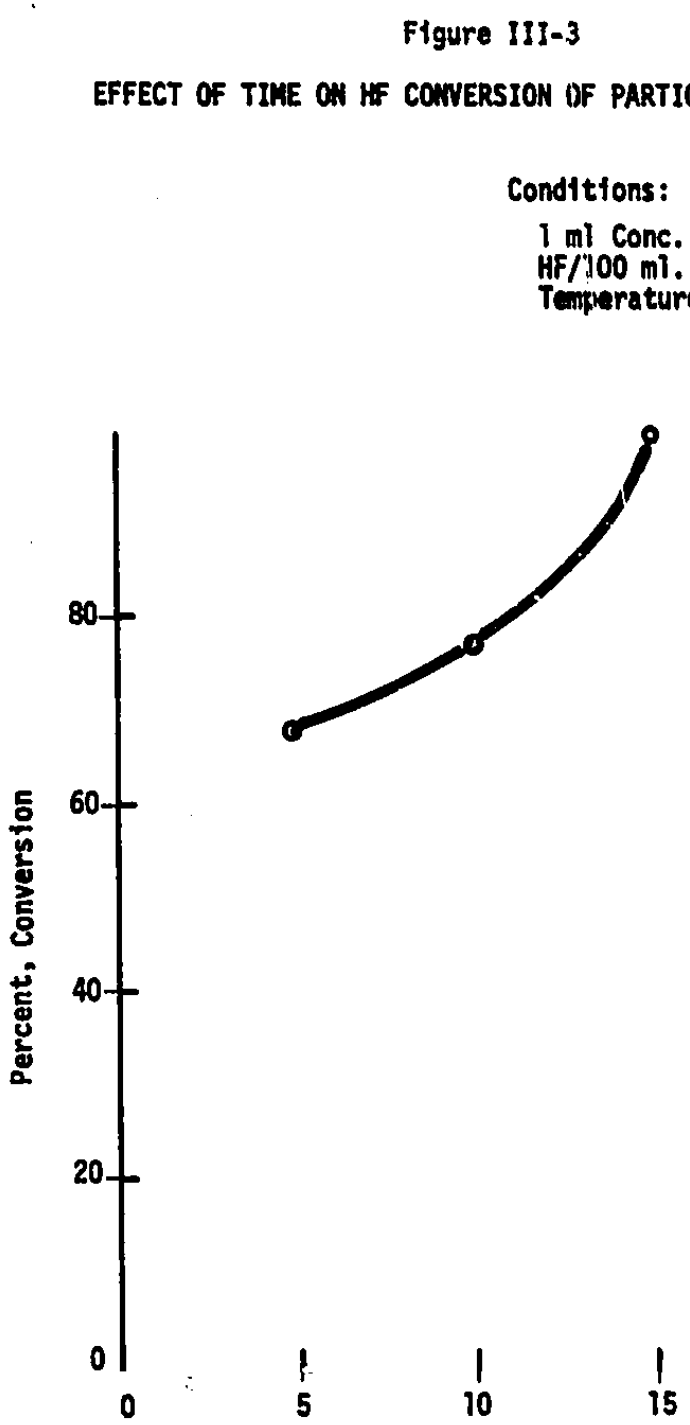
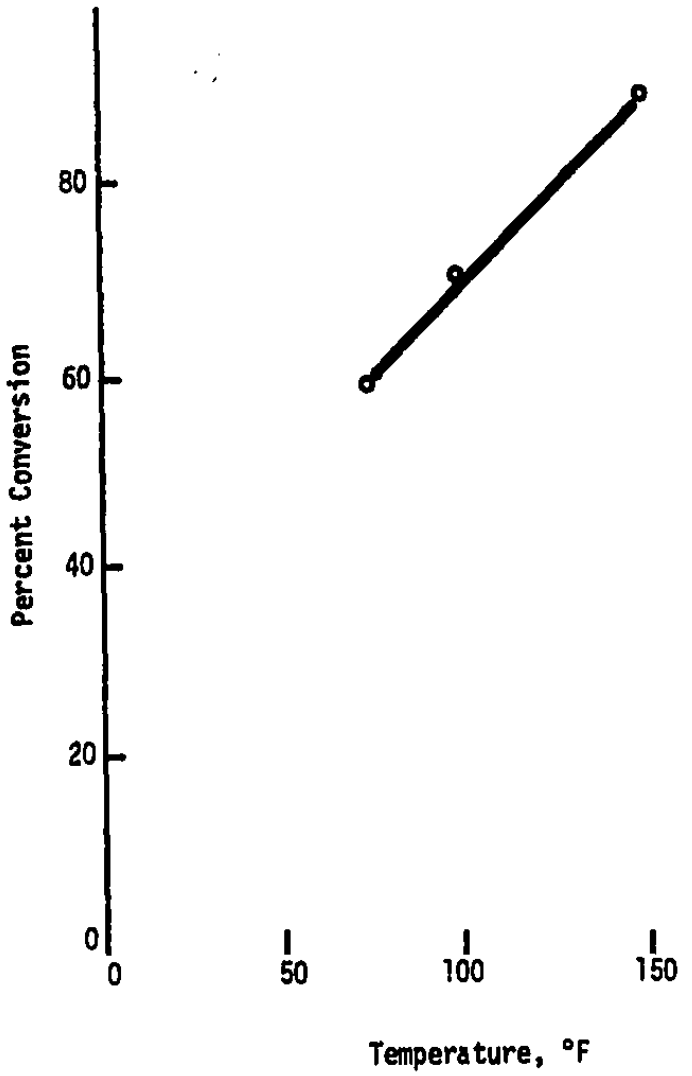


Figure III-4

EFFECT OF TEMPERATURE ON IRON-EDTA CONVERSION OF PARTICULATE TO COMPLEXED COPPER

Conditions:

5 ml. "EDTA Reagent"/100 ml. sample
5 minute contact time



These results indicate that iron-EDTA does convert particulate copper to some other form. Under the conditions cited, it and the ionic copper are chelated with excess EDTA. With copper in the EDTA complexed form, two other requirements, however, must be met before this technique would be useable for a low level copper analyzer.

- The spectral absorption peaks of iron- and copper-EDTA must be separated far enough so one does not interfere with the other.
- Very low concentrations of copper should develop sufficient blue color to give a reasonable absorption of light at the chosen wavelength.

Both of these items were investigated. A spectral transmittance curve was obtained on a mixture of standard iron and copper solutions mixed with ammoniacal EDTA solution. A plot of percent transmittance versus wavelength is shown in Figure III-5. This data shows that the maximum absorption (minimum transmission) of energy for the iron-EDTA complex is at a wavelength of 360 millimicrons while that for the copper-EDTA complex is at 725 millimicrons. The importance of these two numbers is that they are widely enough separated that even a poor spectrometer with a large bandpass will have no trouble "seeing" the copper-EDTA complex. Most moderately priced (<$1,000) spectrometers have a narrow bandpass on the order of 20 millicrons, quite sufficient for our purposes.

From the spectral transmittance curve a point was chosen at a wafelength of 725 millimicrons for preparation of a curve to show the sensitivity and linearity of the spectrophotometric analysis of the blue copper-EDTA complex. Standard copper solutions were prepared and 100 ml. portions of each were treated with 5 ml. of "EDTA Reagent." These solutions were read in a spectrophotometer against 5 ml. of "EDTA Reagent" in 100 ml. of deionized water. The results of this are shown in Figure III-6. These data show that the energy absorption of the copper-EDTA complex is not nearly strong enough to be analytically useful at low copper concentrations. A typical colorimetric analysis should have a much steeper slope, such as the dash line shown in the figure.

Although the data obtained in the range 0 to 10 ppm copper were linear, the light absorption is so low in the parts-per-billion range that no further work on this method was warranted.

Figure III-5

SPECTRAL TRANSMITTANCE CURVE FOR
IRON- AND COPPER-EDTA COMPLEXES

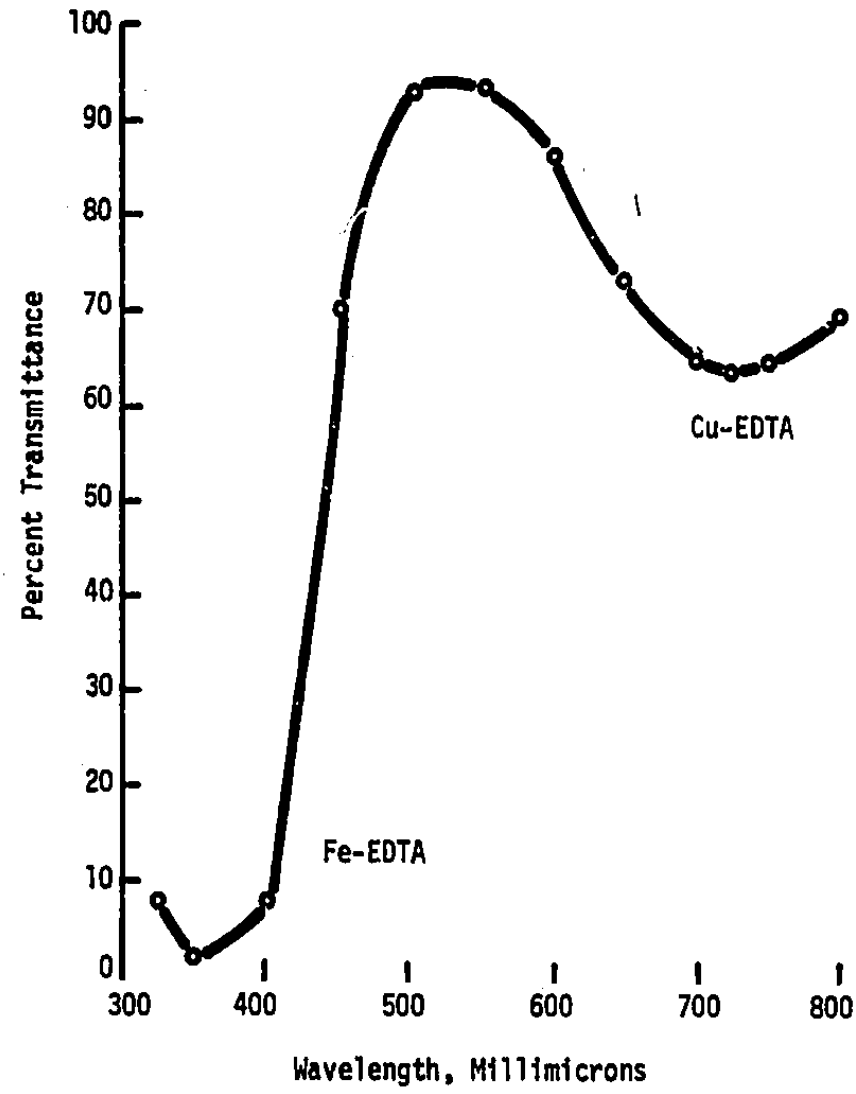
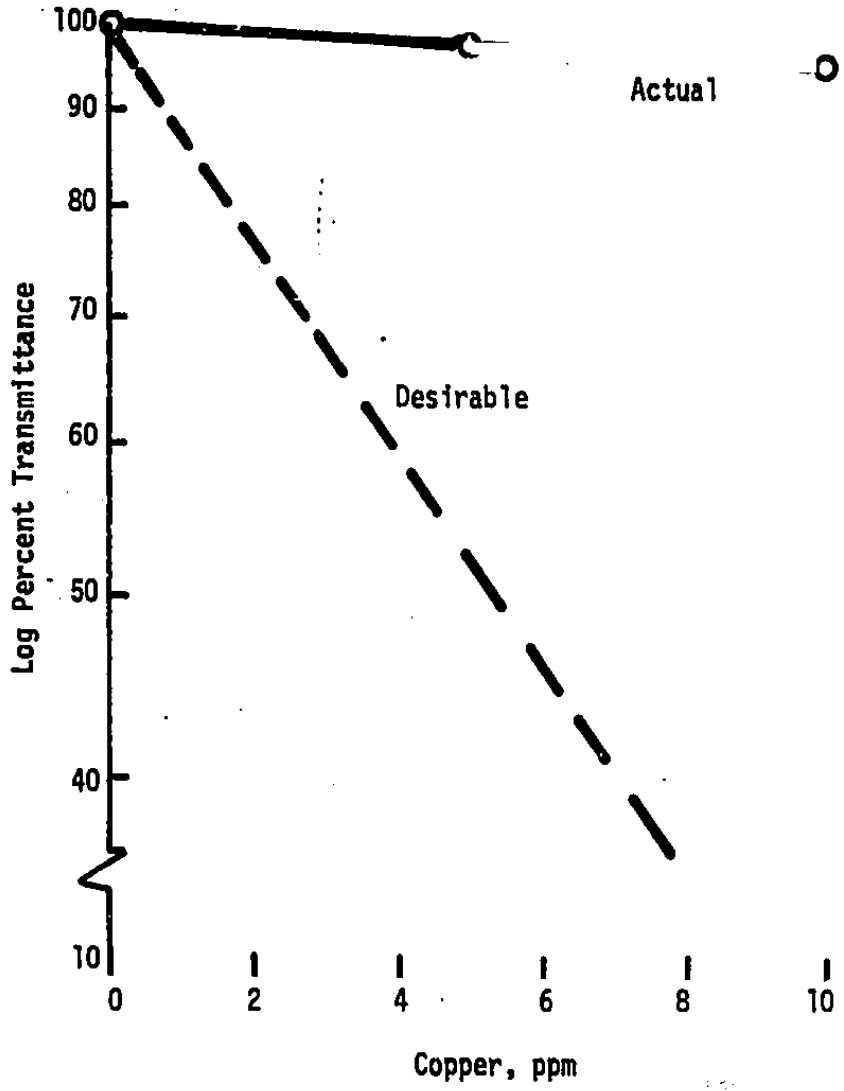


Figure III-6

LIGHT ABSORPTION VS. COPPER CONCENTRATION FOR COPPER-EDTA COMPLEX AT WAVELENGTH 725 MILLIMICRONS



SECTION III. TECHNICAL PROGRAM

C. Chemistry of Carbamate Analysis Method

Based on the results obtained during the acid conversion studies, it was decided that the best approach to obtaining the "total" copper in a sample would be to construct a module for instrumenting the HF-injection technique and use this as a pretreatment for the Hach copper analyzer now on hand. Since this analyzer uses the diethanoldithiocarbamate colorimetric copper analysis, a study of the attendant chemistry was necessary.

Since the pH of seawater following HF-treatment is around 2, the first studies were aimed at finding a pH sensitivity of the carbamate reaction. A standard copper solution was prepared which contained 0.2 ppm copper. Fifty-milliliter portions of this standard were adjusted to various pH values with dilute hydrochloric acid and sodium hydroxide solutions, carbamate reagent added to each, and the mixture diluted to exactly 100 milliliters. After about 10 minutes the percent transmittance of each solution was read on a spectrophotometer. The results of this work are shown in Figure III-7. Inspection of these results show that the carbamate reaction is pH-dependent. The most intense color is produced at about pH 3. Between pH 3 and 6, the intensity falls off, reaching a constant value above pH 6. These results indicate that the most sensitive copper analysis by this method can be performed at pH 3, and the most stable analysis performed at pH 6. Addition of hydrofluoric acid to another series of samples, followed by pH adjustment to various values, gave results identical to those shown in Figure III-7. From these results it was concluded that with proper pH adjustment following the HF-pretreatment, the carbamate method will function properly.

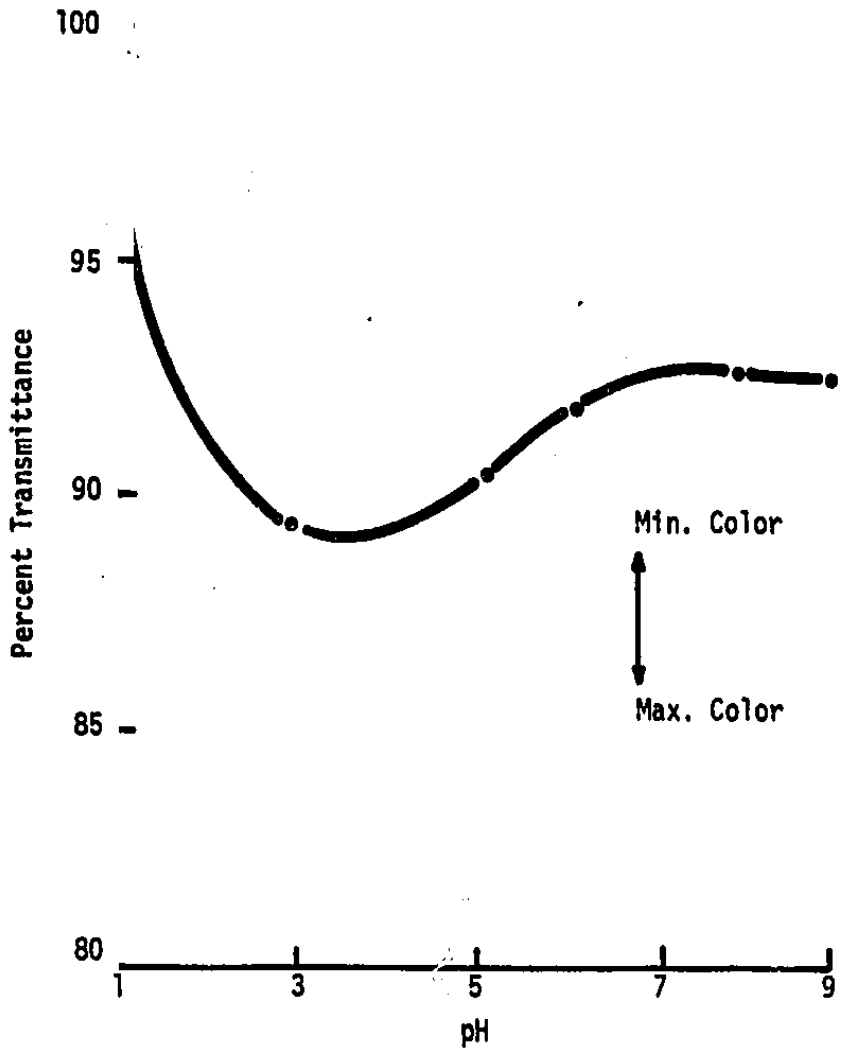
D. Effects of Iron on Carbamate Analysis Method

It was found that the presence of iron causes color intensity of the copper carbamate complex to increase slowly, reaching a stable value after about 7 minutes. Since the waters which will normally be monitored by the finished analyzer will contain iron, it was necessary to contend with this factor.

One hundred-milliliter samples containing 5 ppm iron and 0.5 ppm copper were adjusted to pH 3 and treated with the carbamate reagent. Immediately following the carbamate addition, the percent transmittance of the solution was

Figure III-7

COLOR INTENSITY VS. pH
FOR DIETHANOLDITHIOCARBAMIC ACID
COPPER ANALYSIS METHOD



taken at various times. This data is shown in Figure III-8 (lower curve). Notice that the copper carbamate complex is formed slowly, reaching a stable value after about 7 to 10 minutes.

The reagent scheme in the Hach analyzer uses two reagents, one containing an acetate buffer with sodium pyrophosphate to inhibit iron interference, the other being the carbamate reagent. Either adding pyrophosphate or removing the iron causes the copper carbamate complex to form quite rapidly and reach a steady color intensity immediately. This is shown by the upper curves of Figure III-8.

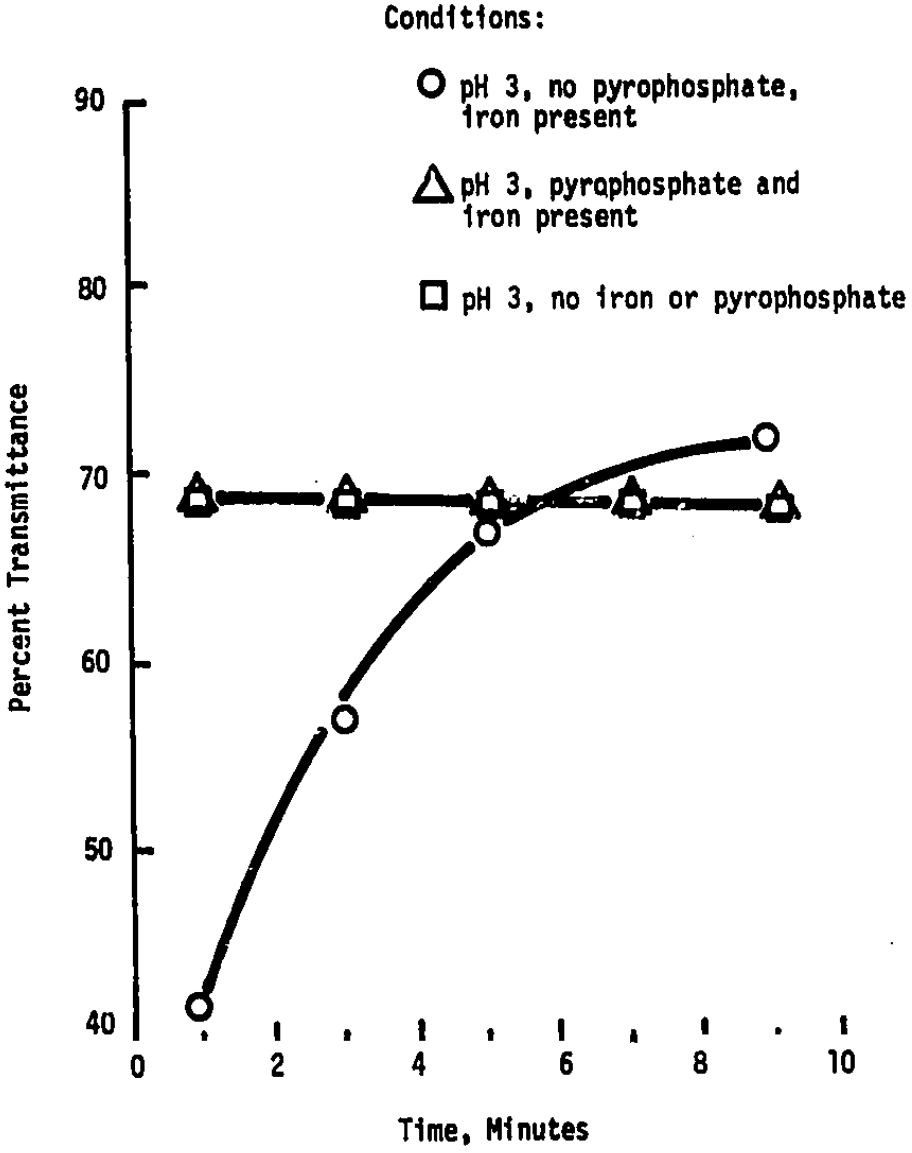
From the foregoing one might conclude that it is only necessary to precede the Hach analyzer with the HF-pretreatment step, iron being taken care of by inclusion of pyrophosphate in the buffer solution. However, this is not the case. Upon addition of the Hach Reagent I to the acid-treated seawater, a precipitate forms which creates a turbid water condition. The addition of either pyrophsphate or the acetic acid-acetate buffer causes this same turbidity in seawater samples which have been acidified with hydrofluoric acid. The addition of either or both of the above constituents to seawater containing no hydrofluoric acid does not result in turbidity formation. Precipitate formation thus makes the HF-pretreatment step and the Hach copper analyzer chemistry incompatible.

Since in all previous work the HF-acidification has proved to be the most effective means for converting all three forms of copper to a form which will react with the carbamate reagent, it was necessary to modify the Hach analyzer chemistry to make it compatible with the HF treatment. The simplest approach was the selection of another buffer system to raise the sample to the required pH. This new buffer ideally should also contain citrate ion which keeps iron from interfering, in lieu of pyrophosphate ion as used in the Hach reagent.

Various buffers were added to HF-treated seawater to determine which buffer would raise the pH to above 5 or 6 and still leave the solution devoid of turbidity. Solutions of sodium phosphate, sodium bicarbonate, sodium borate, acetic acid-sodium acetate, sodium citrate, ammonium hydroxide, ammonium hydroxide-ammonium chloride, and triethanolamine were all found to cause the turbid condition in the HF-treated seawater samples. A satisfactory

Figure III-8

EFFECT OF IRON ON
DIETHANOLDITHIOCARBAMIC ACID
COPPER ANALYSIS METHOD AT LOW pH



buffer was a 50 to 75 percent solution of citric acid neutralized with ammonium hydroxide to pH 9. This reagent raised the sample to pH 6. As the reagent is added to the sample, a point is reached where slight turbidity forms but disappears as the pH rises above 5. Since this analysis process is of a continuous nature with the sample remaining above pH 5, the turbidity problem was solved and was no longer a factor in the analysis.

E. Alternate Colorimetric Analysis Scheme

An alternate copper analysis similar to the diethanoldithiocarbamate involves the use of dibenzyldithiocarbamate at pH 2. Reportedly, at this pH, the reagent is very specific for copper, with no iron interferences. Since the HF-treated samples end up at pH 2, it was necessary to study this method. The alternate reagent was found to be insoluble in water and the lower alcohols. Since the instrumentation on hand does not provide for operation by extraction of the colored copper complex into an organic medium, this reagent would not be practical for use in lieu of the original carbamate. The reagent was tested on copper standards by adding a carbon tetrachloride solution of the dibenzyl carbamate to portions of the standards treated with hydrofluoric acid to pH 2 and extracting the complex into the organic phase. The method was quite sensitive at low levels of copper. However, since the method by necessity involves extraction into an organic solvent, no further work was done on this reagent.

F. Instrumentation of Hydrofluoric Acid Injection

A flow-through mixing chamber for hydrofluoric acid-seawater contact was built consisting of a closed cylinder with inlet and outlet connections and a perforated plate across the center cross-section of the cylinder. All parts were made of Plexiglas® acrylic plastic. The cylinder contains a magnetic stirring bar. The center plate is required to eliminate the vortex caused by stirring, thereby reducing concentration streaming in the mixing chamber.

A variable speed peristalic tubing pump is used for the acid injection. The sample flow to the mixing chamber is controlled by a ball valve and monitored with a rotameter.

This apparatus was set up at the OSW Materials Test Center. A sample line from a corrosion test unit was run to the apparatus in order to provide a continuous supply of sample.

Concentrated hydrofluoric acid (49%) was diluted 1:10 with deionized water and injected into the sample stream at 3 ml./minute. Sample flow was 100 ml./minute.

Samples were collected before and after the mxing chamber for copper analysis. It was found that for a sample pH of about 7 to 8 the pH after HF injection was 2 to 3. Rates of copper conversion (particulate to ionic) on many different trials were found to be in the range 60 to 100% conversion. Most of the rates were in the 85 to 100% range when corrected for the analytical "reagent blank."

After several hours of run time, it was evident that silica was depositing on all surfaces of the mixing chamber, especially the top side of the perforated baffle. Several holes in the baffle were plugged. Silica plugging at the acid entrance point was also experienced.

Since the silica deposit was sticky and adherent to the surfaces of the plastic chamber, it was decided that other materials of construction would be investigated. In this regard, a Teflon® baffle was made and installed in the chamber.

After operating several hours, the baffle was inspected and found to be essentially free of silica deposits. All holes in the baffle were unplugged although a small amount of deposit was noted around the holes. A Teflon® baffle was, therefore, permanently incorporated into the mixing chamber.

In addition to silica buildup problems in the mixing chamber, problems were also encountered at the acid entrace point. Silica deposits were found to plug the tee in the sample line, the point of acid addition. This problem was corrected by adding the acid to the sample in the mixing chamber. The high velocity due to stirring keeps silica from plugging the acid injection point. No further problem was experienced from silica.

G. Secondary Treatment-Sample Filtration

After treatment of a sample with HF, the water is still turbid. This turbidity is attributed to silica ($SiO_2$).

Before a sensitive colorimetric analysis can be performed, this turbidity must be either removed or compensated for.

The previously described flow-through mixing chamber was set up to be followed by a cartridge filter holder. Samples before and after this holder were collected and turbidity (suspended solids) readings made on a Klett-Summerson colorimeter.

Various felt and plastic filters were tried, each having a different pore size. Zero turbidity was chosen to be that amount remaining after passing the sample through a 0.45-micron membrane filter.

The results of this work in the range up to a 10-micron filter are shown in Figure III-9. The shape of this curve is as expected. Filters of 2-micron pore size and smaller become very effective for removing the suspended solids present.

Based on this data, a 1-micron filter was chosen for further study. It was found that after an initial "break in" period of about 30 minutes, the water leaving the filter was quite clean (colorimeter reading 6). After the filter had "aged" for an hour, the colorimeter reading had dropped to 3 and did not improve beyond this.

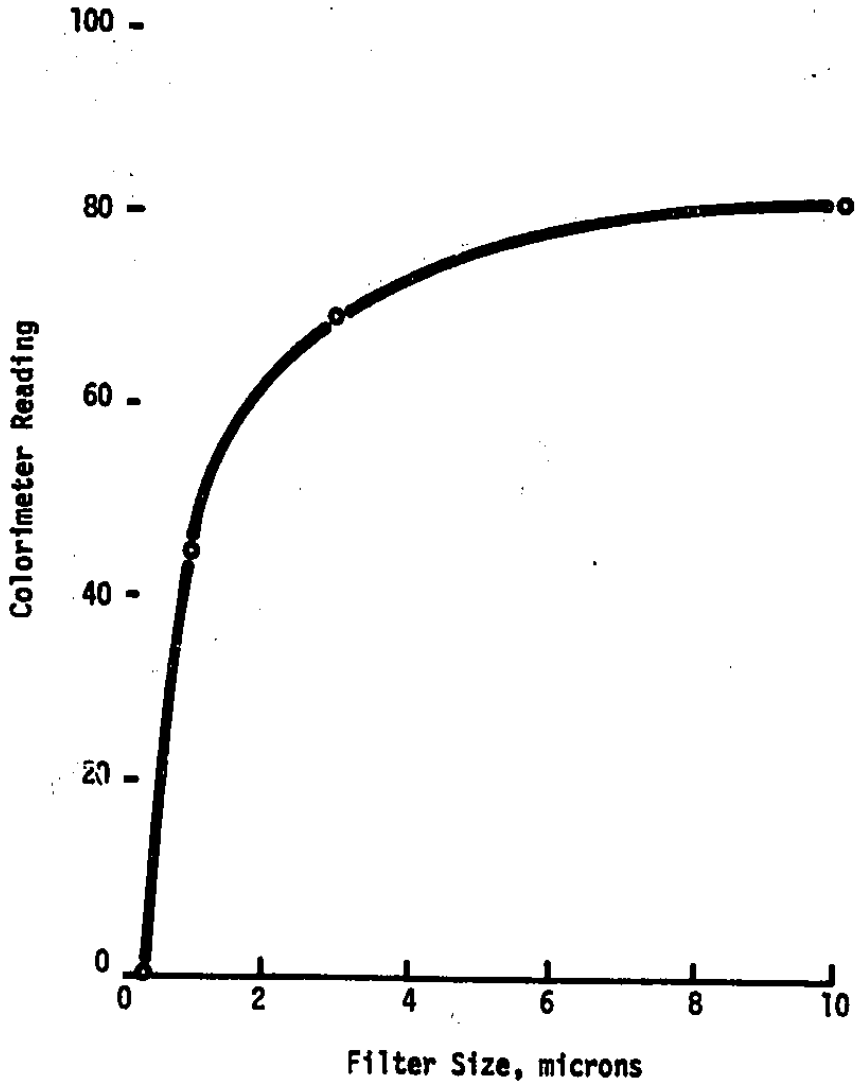
After an operating period of 20 hours, the filtered sample remained clear. The filter showed no signs of plugging as no back-pressure had developed. Inspection of the filter revealed a uniform coating of solids on the outer surface. This coating was easily removed by simple washing.

It was noticed that the silica causing the turbidity always accumulated on the surface of the filter and did not actually penetrate into the filter element itself. The filter cartridge evidently was only providing a surface for the silica to cling to.

Based on the idea that only a large surface area is required and not a specific pore size, a filter was constructed by filling a plastic container with glass wool. This filter was attached to the HF mixing chamber. Subsequent tests showed that the sample effluent from the filter was completely clear. All traces of silica had been removed. The glass wool was removed and studied under a microscope. As expected the surface of the glass was found to be coated with silica and severely etched by the hydrofluoric acid.

Figure III-9

TURBIDITY VS. FILTER SIZE
FOR HF-TREATED SAMPLE



The glass wool was replaced with medical grade cotton and the filter element again attached to the HF mixing chamber. The cotton was as effective as the glass wool, as all silica was easily removed to leave a very clear sample. Inspection of the cotton showed no effect from the HF.

The use of such a filtration system is much more desirable than a cartridge filter element due to the availability and low cost of such a system. The cotton packing is also more easily replaced than a cartridge filter element, lending itself quite nicely to the routine maintenance required in this area of the analyzer.

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NOTE: The continuous copper analyzer in this and following sections, referred to as the Hach analyzer, is manufactured by Hach Chemical Company, Ames, Iowa.

## SECTION IV. ASSEMBLY AND TESTING

### A. Design and Construction

Based on the results described in Section III, a pretreatment module was designed to convert the copper to a common form and remove the turbidity from the sample. A simplified flow diagram of the chosen analytical system for monitoring "total" copper was shown in Figure II-1 (p. 3).

Based on this analytical scheme, the pretreatment module was designed with the following features:

1. Use of plastic parts to prevent hydrofluoric acid attack

2. Use of the cotton filter already described

3. Incorporation of design for ease of cleaning and maintenance

4. Use of readily available parts for construction and replacement

5. Incorporation of maximum user safety

The pretreatment module was constructed in a steel electrical utility box with a removable interior plate. The various components are fastened to this plate. The module is shown in Figure IV-1. The top of the assembly contains a Plexiglas® tank of 1.3-gallon capacity for storage of the 4.8 percent hydrofluoric acid. At the lower left a variable speed peristaltic tubing pump is located. Note that the pump is inverted in order to protect its electrical circuits in the event of a tubing leak. The mixing chamber and cotton filter are located to the right of the pump.

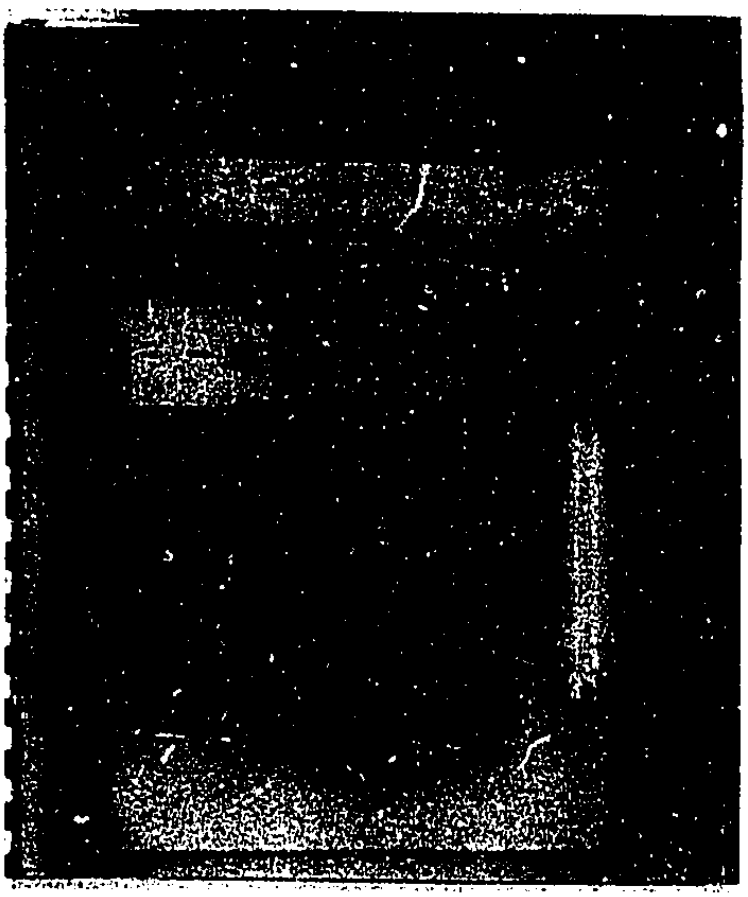
The injection point for the hydrofluoric acid has been placed through the wall of the mixing chamber rather than into a tee in the sample line.

All vessels are interconnected with Tygon® tubing and quick-disconnect fittings. This facilitates removal and cleaning of all components.

Module size was chosen with ease of adjustment and manipulation in mind during the testing phases of the program. It is possible that the module can be reduced in size to

Figure IV-1

HYDROFLUORIC ACID PRETREATMENT MODULE



about half that shown and incorporated into the Hach analyzer cabinet.

Several modifications were made to the Hach copper analyzer in order to make it more suitable for our purposes. The buffer system used in the analyzer was changed as outlined in Section III. The point of addition of the buffer solution was changed to correct a capillary plugging problem. In the original analyzer, the buffer was added to the sample stream at a very low velocity point. When the change in the buffer system was made, this caused the capillary to plug due to the increased concentration of the buffer. In order to correct this difficulty, the analyzer was modified to contain a small plastic vessel, magnetically stirred, into which the capillary which delivers the buffer was placed. The increased velocity due to stirring in this vessel corrected the capillary plugging problem.

In addition to correcting the plugging problem, this vessel more effectively mixes the buffer into the sample stream, thereby reducing schlieren which were entering the colorimetric cell, causing a minute "wavering" of the recorder baseline because of the changing refractive index in the cell.

It was noticed early in the program that the photocells of the colorimetric analyzer had a rather short life. The photocell bridge is contained on a constant temperature block which is electronically controlled by a thermistor and transistor voltage controller. It was suspected that the temperature was too high, causing the photocells to rapidly deteriorate. In order to correct this problem, a 220,000 ohm resistor was placed in parallel with the thermistor, which lower the block temperature from 62 to 50°C. No further problems have been experienced with the photocells. No loss in sensitivity was evident.

The HF pretreatment module was placed in the sample line ahead of the Hach copper analyzer. A strip-chart recorder was connected to the analyzer, thus completing the assembly. Figure II-2 shows the completed analyzer. On the left is the pretreatment module. Notice that a plastic tray has been added in the bottom of the case. This was found necessary to catch any spills as the various components are removed for cleaning. On the right is the Hach analyzer. The stirrer and new buffer mixing system can be seen to the left in its cabinet.

SECTION IV. ASSEMBLY AND TESTING

B. Operation

Due to the nature of the chemicals involved, extreme care should be exercised during preparation of the required reagents and filling of the storage tanks, etc. It is suggested that the chemical goggles and protective gloves be worn during all operations involving handling the reagents.

1. Reagent Preparation

   a. Prepare the dilute hydrofluoric acid by mixing reagent grade HF with deionized water in the ratio one to nine by volume. Always add the acid to the water.

   b. Prepare the buffer solution by mixing a 50% by weight reagent grade citric acid solution in deionized water with reagent grade ammonium hydroxide until the pH of the mixture is 9.0.

2. Changing Pump Tubing

   When changing the pump tubing, it is suggested that chemical goggles and gloves be worn. Shut off the supply of HF to the pump tubing. Disconnect the old tubing at each end. Rinse the tubing with water and discard. Reconnect the new tubing and again turn on the HF supply.

3. Routine Start-Up

   a. Verify that all tubing connections are sound.

   b. Turn on HF storage tank valve.

   c. Start sample flow and adjust flow to pretreatment module to 100 milliliters per minute.

   d. Turn on magnetic stirrers and tubing pump.

   e. Adjust tubing pump to 3 milliliters per minute.

   f. Start buffer and Hach reagent "Copper II" flow in the colorimetric analyzer.

   g. Follow manufacturer's directions for calibration and operation of the Hach instrument.

4. Routine Shut-Down

   a. Shut off tubing pump and magnetic stirrers.

   b. Shut off Hach instrument reagent flows.

   c. Valve off HF storage tank.

   d. Shut off sample flow to pretreatment module.

C. Testing

The instrument was first set up at the OSW Materials Test Center at Freeport, Texas. One of the OSW corrosion test units not being used at the time was loaded with copper coupons. It was possible to vary the amount of dissolved oxygen to the loop and thus vary the amount of copper coming from the loop. The dissolved oxygen content to the loop was monitored continuously.

Samples of the feed to the loop were taken for dissolved oxygen analysis. Samples of the blowdown from the loop were taken for total copper analysis by the conventional laboratory procedure and by the continuous copper analyzer. The amount of oxygen entering the loop was monitored and was recorded. The results from several of the tests made are shown in Table IV-I. Notice that the analyzer shows very good agreement with the wet chemical copper analyses, especially as a copper concentration is reached which is typical of that found in the samples normally encountered.

In order to show that the analyzer would show changes in copper corrosion rate, the oxygen to the loop was increased to a higher value. The copper analyzer responded to such a change in about a 5 minute period, lining out very nicely at the higher copper level experienced at the higher corrosion rate. This data is shown in the recorder chart traces of Figure IV-2. The oxygen concentration was increased from 76 ppb to 144 ppb, resulting in a change in copper from 0.10 ppm to 0.20 ppm. This data shows that the analyzer is quite useful for seeing a change in copper in a sample stream due to a change in conditions in the source of the sample stream.

In order to check the interference of iron, as discussed in Section III, a stable copper reading on the analyzer was obtained. One milliliter of a 1,000 ppm iron standard was injected into the sample line leading to the analyzer. The analyzer response changed by an amount equivalent to

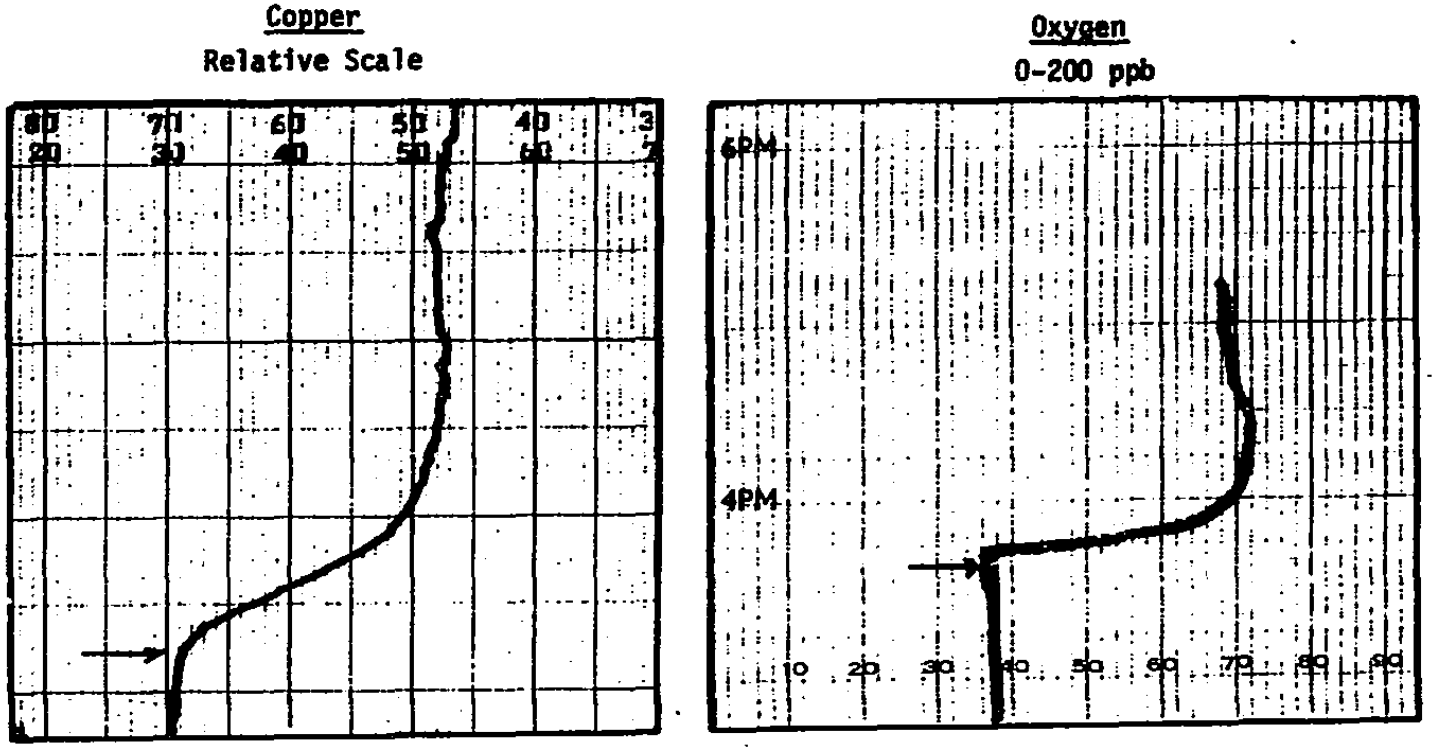
Table IV-I

COPPER ANALYZER RESULTS FROM OSW UNIT

| Data Point | Dissolved Oxygen, ppb | Wet Copper, ppm Cu | Analyzer, ppm Cu |
|---|---|---|---|
| 1 | 180 | 0.15 | 0.12 |
| 2 | 180 | 0.11 | 0.10 |
| 3 | 330 | 0.22 | 0.21 |
| 4 | 370 | 0.30 | 0.26 |
| 5 | 370 | 0.30 | 0.26 |
| 6 | -- | 0.92 | 0.89 |
| 7 | -- | 0.03 | 0.04 |
| 8 | -- | 0.03 | 0.03 |
| 9 | -- | 0.02 | 0.03 |
| 10 | -- | 0.02 | 0.03 |
| 11 | -- | 0.03 | 0.03 |
| 12 | -- | 0.01 | 0.02 |

Figure IV-2

COMPARISON OF COPPER CORROSION RATE
AND DISSOLVED OXYGEN CONCENTRATION



less than 0.005 ppm copper, a very insignificant amount for the amount of iron added. In a similar manner, the effect of a large pH upset in the sample to the analyzer was determined. One milliliter of concentrated hydrochloric acid was injected into the sample line. This is really an exagerated change in pH. The instrument response changed by an amount equivalent to less than 0.01 ppm copper. From this data it was concluded that iron in the sample and changes in pH are not detrimental to accurate operation of the analyzer.

The data obtained in the OSW corrosion unit was further supported by installation of the analyzer at the OSW Freeport, Texas Test Bed Plant. The analyzer was connected to the final brine from the last effect of the plant. Wet-chemical copper analyses were made as a check on analyzer performance. The results were essentially as already seen. The analyzer was in all cases very close to the value found by chemical analysis. On several occasions a rapid change in copper concentration was related to a change in plant operating conditions made at about the time predicted by the analyzer. Changes in temperature, pH, dissolved oxygen, and addition of chlorine all resulted in changes in copper concentration which were readily seen by the analyzer. Any changes in the deaeration/decarbonation tower operation were quickly monitored by the analyzer.

## SECTION V. APPENDIX A - PROCEDURE FOR COPPER ANALYSIS

### A. Scope

Ionic, complexed, and particulate copper in the parts-per-billion range in seawater and brines may be determined by this method.

### B. Principle of Method

Copper in the sample is reduced to the cuprous form with hydroxylamine hydrochloride. The resulting cuprous ion is then able to form a yellow colored complex with 2, 9-dimethyl- 1, 10-phenanthroline (neocuproine). A buffer solution of sodium citrate produces a pH of 6 prior to this complex formation. The copper-neocuproine complex is extracted from the aqueous phase with chloroform.

The intensity of the colored complex in the organic phase is proportional to the concentration of copper in the sample, the intensity being determined with a colorimeter. The concentration of copper in the sample is determined from a previously prepared calibration curve.

### C. Interferences

Substantial amounts of chromium and sulfide can interfere with this method. Such interferences are normally not found in the samples being analyzed.

### D. Apparatus

1. A filter colorimeter with a blue filter having maximum transmission at 457 mμ is used to measure the intensity of the complex. A 4-cm path-length cell is utilized.

2. Normal laboratory glassware.

### E. Reagents

All reagents are prepared in distilled, doubly deionized water.

1. Neocuproine -- 0.1% solution in "2B" ethanol

2. Hydroxylamine hydrochloride -- 10% solution

3. Sodium citrate -- 25% solution

4. Potassium persulfate -- 0.1 N $K_2S_2O_8$

5. Standard copper solution -- 1.0000 gm. electrolytically pure copper dissolved in nitric acid and dilute to one liter (1 ml. = 1 mg. Cu)

F. Sampling

Samples are collected in polyethylene bottles and analyzed immediately.

G. Calibration Curve

Prepare a calibration curve by analyzing aliquots of standard copper solution covering the range 0-250 µg Cu by the procedure for ionic copper. Plot on semilog paper percent transmission (log axis) vs. µg Cu (linear axis).

H. Procedure

1. Ionic Copper

a. Filter a suitable size sample through a 0.45-micron membrane filter. Rinse filter with de-ionized water and save for particulate copper analysis.

b. Quantitatively transfer filtrate to separatory funnel and add 2 ml. hydroxylamine hydrochloride, 25 ml. sodium citrate, 5 ml. neocuproine, and 15.0 ml. chloroform. Shake vigorously and allow layers to separate.

c. Draw off the chloroform layer through a No. 41 Whatman filter paper into the colorimeter cell.

d. Measure the color intensity of the chloroform against a similarly run reagent blank and determine copper from calibration curve.

2. Complexed Copper

a. To the same size filtered sample as for ionic copper add 2 ml. potassium persulfate and 1 ml. concentrated hydrochloric acid. Bring to boil and reflux in a 500 ml. volumetric flask for ten minutes. Cool and determine copper as before.

b. Subtract ionic copper from that found above to obtain complexed copper.

3. Particulate Copper

a. Place the filter from one of the above filtrations in a platinum crucible, wet the filter with acetone, and ignite. When burning is complete, heat the crucible to glowing over a Meeker burner. Cool, add a few milliliters of concentrated hydrofluoric acid, a few drops of concentrated sulfuric acid, and evaporate to dryness on a warm hot plate. Cool, add about 1 ml. concentrated hydrochloric acid, and warm to dissolve any residue.

b. Transfer to a separatory funnel and proceed as for ionic copper.

I. Precision

Results are reproducible to about ±5% of the amount of copper present.